Sulphur Release in Technogenic Soil Substrates: Experiments and Numerical Modelling

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Abstract

In Berlin and many other cities technogenic soil substrates, in the form of World War II debris, play an important part as substrate for soil formation. The biggest debris landfill site in Berlin is the Teufelsberg. Many of the materials contain high amounts of sulphur, often in the form of sulphate. The sulphate release poses a threat for groundwater resources.

The scope of this study was to determine the processes controlling sulphate release. Processes influencing release are adsorption, dissolution, precipitation and transport. To investigate these five column leaching experiments with fine soil from a middle slope of the Teufelsberg were carried out, one of these experiments was undertaken with sulphate as a tracer to investigate sulphate sorption. During experiments flow interruptions of one and seven days were introduced. Ideal tracer signals of potassium-bromide were used to determine transport parameters and to investigate whether physical non-equilibrium was important. No physical non-equilibrium was observed. Inflow of sulphate rich solution showed no adsorptive effects for sulphate.

Using the data a model was set up using a geochemical simulation tool (HP1, a merge of Hydrus 1D and PHREEQC). The model considered water flux, solute transport, first order kinetics and precipitation/dissolution. The experimental results were qualitatively described by the model. The calculated equilibrium constant for gypsum was a factor of 1000 smaller than expected. It is assumed that the mobilisation of sulphate from calcite/gypsum co-precipitates determines the sulphate concentrations in the soil solution of the studied soils.
Eidesstattliche Versicherung


Berlin am 12.05.2011

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Horst Schonsky
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### Nomenclature

The units given here are SI units. The units of the constants used in the numerical models depend on the units chosen in the models. For the modelling cm were applied as spatial unit, h as temporal and mol for mass.

<table>
<thead>
<tr>
<th>Variable/Parameter</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ ]</td>
<td>mol/m³</td>
<td>Concentration of a given species</td>
</tr>
<tr>
<td>{ }</td>
<td>mol/m³</td>
<td>Activity of a given species</td>
</tr>
<tr>
<td>( A )</td>
<td>-</td>
<td>Temperature dependant parameter of the Debye-Hückel equation</td>
</tr>
<tr>
<td>( a )</td>
<td>-</td>
<td>Stoichiometric coefficient for species A in a chemical reaction</td>
</tr>
<tr>
<td>( A )</td>
<td>mol/m³</td>
<td>Placeholder for a species in a chemical reaction</td>
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<tr>
<td>( A )</td>
<td>Å</td>
<td>Adjustable parameter, corresponding to ion radius</td>
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<td>( A_0 )</td>
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<td>( B )</td>
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<td>( c_{i} )</td>
<td>mol/m³</td>
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</tr>
<tr>
<td>( c_{i,j} )</td>
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<td>Concentration of species ( i ), measurement ( j )</td>
</tr>
<tr>
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<td>mol/m³</td>
<td>Predicted (simulated) concentration of species ( i ), measurement ( j )</td>
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<td>Total concentration of species ( i ) per volume of soil</td>
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<td>( D_e )</td>
<td>m²/s</td>
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<tr>
<td>( D_L )</td>
<td>m</td>
<td>Longitudinal dispersivity</td>
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<tr>
<td>( f_i )</td>
<td>-</td>
<td>Activity coefficient of species ( i )</td>
</tr>
<tr>
<td>( h )</td>
<td>m</td>
<td>Pressure head</td>
</tr>
<tr>
<td>( I )</td>
<td>-</td>
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</tr>
<tr>
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<tr>
<td>( J_d )</td>
<td>mol/m²/s</td>
<td>Diffusive solute flux of a species</td>
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### Sulphur Release in Technogenic Soil Substrates

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<th>Unit</th>
<th>Description</th>
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<tr>
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<td>Solute flux of species $i$ through a given cross section</td>
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<tr>
<td>$J_w$</td>
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<td>$k_{ad}$</td>
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<td>Linear adsorption coefficient</td>
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<tr>
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<td>Thermodynamic equilibrium constant for a given reaction.</td>
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<td>$k_{kin}$</td>
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<td>Rate constant</td>
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<td>$k_u$</td>
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<tr>
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<td>Effective soil water saturation</td>
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<td>Source/sink term for species $i$</td>
</tr>
<tr>
<td>$t$</td>
<td>s</td>
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<tr>
<td>$\rho_b$</td>
<td>g/m³</td>
<td>Bulk density of soil</td>
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1 Preface

I like to use this space to thank a number of people who guided me during this work, gave me helpful advice or just listened to hours of moaning.

First of all I want to thank Andre Peters and Fritzi Lang for their clear and helpful role as academical advisors, also for very good input and for long discussions about the topic. Beate Mekiffer helped me to find my way into sulphur dynamics and understanding the previous studies undertaken at the department. Enrico Hamann from the Workgroup Hydrogeology (FU Berlin) really did give me a kick start for working with and understanding PHREEQC code. Without him first steps would have taken much longer.

I also want to thank Prof. Dr. Wessolek for the warm welcome at the department of “Standortkunde und Bodenschutz” and help in overcoming planning difficulties. Till and Andreas helped me a lot in realising experiments and chemical analysis, without them the experimental foundation of this work would not have been possible to this extend.

Marcus Bork takes a special place for listening to hours of meaningless babbling about thermodynamics, kinetics and beer.

Last but not least my I want to thank my girlfriend Antje for being there during a difficult period, while writing a major work herself.
2 Introduction

The most common sulphur species in soils is sulphate ($\text{SO}_4^{2-}$). As sulphur is essential for life it is widely studied [Lindsay, 1979]. Its reactions in soils are closely associated with organic matter. Sulphur also occurs in many oxidation states and redox reactions have to be considered if no free oxygen is present [Lindsay, 1979].

This work concentrates on the dynamics of sulphate. Sulphate is of interest for drinking water treatment because of its corrosive properties [TrinkwV, 2001], [Nissing, 2004]. In Germany sulphur content is regulated in the regulation for drinking water (“Trinkwasserverordnung”, abbr.: TrinkwV), the legal limit for sulphate is 240 mg/L, geogenic concentrations up to 500 mg/L are tolerable [TrinkwV, 2001]. Background concentrations up to 200 mg/L are found in Brandenburg [Kunkel et al., 2003] cited by Fugro (2006). In Berlin sulphur concentrations are generally higher. This is attributed to World War II debris, which is distributed all over the town, as it was dumped wherever possible after the war. Also landfills were put up with this debris. The biggest is the Teufelsberg in Berlin. The problem of high sulphur concentrations is well illustrated by a measurement well in which sulphur levels of 50 mg/L were reported in the fifties [Siebert, 1956] cited in Fugro (2006), whereas 40 years later values of over 400 mg/L were reported [GCI, 1998] cited in Fugro (2006).

As the Teufelsberg seems to be a major source of sulphate in the groundwater, it is of interest how sulphur is released from technogenic soil substrate. Jang and Townsend (2001) studied the leaching of sulphate from recovered construction and demolition debris fines (fraction $<9.5 \text{ mm}$). During column experiments they found sulphate concentrations of up to 2200 mg/L. This is far above the solubility limit for pure water (which is about 1000 mg/L). In solutions with high ionic strength much higher equilibrium concentrations can be found (up to five times higher) [Bock, 1961]. This explains concentrations higher than equilibrium concentrations for pure water.

The aim of this work is to examine the release of sulphur by material taken from the Teufelsberg. The processes of sulphate release are not studied on a micro but on a macro scale (i.e. $\sim 1 \text{ dm}^3$). Identification and effective description of these processes is the aim. To achieve this column experiments were carried out and the experiments were compared to numerical models.
3 Theory

Sulphur dynamics in soils is influenced by a wide array of processes. To understand and model sulphur dynamics, these processes have to be understood and mathematically described. This chapter deals with the basic concepts used for the mathematical description of the experimental results and contains the characteristics of gypsum (CaSO$_4\cdot$2H$_2$O). Gypsum is assumed to be the main source for sulphate from technogenic soils. As will be elaborated in Chapter 4.1.3, the columns were at all times not saturated with water. Therefore O$_2$ was at all times present and no redox reactions were expected to take place, therefore they will not be described here. Mechanisms to describe the processes are: Water flow, solute flux, dissolution/precipitation, sorption and kinetics. The theoretical model for these processes will be briefly discussed in this chapter.

3.1 Water Flow

In the experiments water flow conditions were arranged to be steady state with a unit gradient. Steady state water flow under unsaturated conditions is described by the Buckingham-Darcy equation:

$$J_w = -k_u(h) \left( \frac{\partial h}{\partial z} + 1 \right).$$  \hspace{1cm} (3.1)

$J_w$ is the water flow, $k_u(h)$ the unsaturated water conductivity, $h$ the pressure head and $z$ the spatial coordinate (positively defined upwards).

The unsaturated water conductivity is dependent on water content of the soil. The effective soil water content ($S_e$) itself is a function of the pressure head $h$. It is often described by the van Genuchten equation:

$$S_e(h) = \frac{1}{\left[1 + \left(\frac{\alpha}{h} \right)^n\right]^m},$$  \hspace{1cm} (3.2)

where $\alpha$ and $n$ are fitting parameters and $n > 1$. The definition of $m$ is:

$$m = 1 - \frac{1}{n}.$$  \hspace{1cm} (3.3)

To transfer the actual soil water content $\theta$ into the effective soil water content ($S_e$). The definition of $S_e$ is:
\[ S_e = \frac{\theta(h) - \theta_i}{\theta_s - \theta_i}. \]  

(3.4)

Where \( \theta_s \) is the saturated water content and \( \theta_i \) is the residual water content. For Equation (3.2) the predictive capillary bundle model of Mualem has the following analytical solution for the unsaturated water conductivity \( (k_u) \):

\[ k_u(S_e) = k_s \cdot S_e^l \left[ 1 - (1 - S_e^{1/m})^m \right]^2, \]  

(3.5)

where \( l \) is a parameter taking into account tortuosity and connectivity. The saturated water conductivity is \( k_s \).

With this bundle of equations steady state water flow for a fixed pressure head is described.

### 3.2 Solute Dynamics

To mathematically describe the solute dynamics found in the experiments of this thesis three processes and kinetics need to be considered. The processes involve how matter is transported and how it interacts with the soil matrix. The interactions described here are sorption and dissolution/precipitation. Transport and matrix interaction are influenced by reaction kinetics. The kinetics dealt with here is just applied to dissolution and precipitation.

These topics make up the sections found in this chapter (transport, sorption, dissolution/precipitation and kinetics).

#### 3.2.1 Solute Transport

One of the most important equations in this work is the advection dispersion equation (ADE). It governs how matter is transported in the system. This means the conditions under which sorption, precipitation and dissolution take place are calculated from the ADE.

\[ \frac{\partial(\theta \cdot c_i + \rho_b \cdot q_i)}{\partial t} = - \frac{\partial}{\partial z} \left( J_w \cdot c_i - \theta \cdot D_e \frac{\partial c_i}{\partial z} \right) - S_i \]  

\[ \theta \] is the water content of the soil, \( c_i \) the concentration of species \( i \), \( \rho_b \) the bulk density of the soil, \( q_i \) the adsorbed concentration of the species \( i \) and \( t \) the time coordinate. \( z \) is the spatial coordinate, \( J_w \) the water flux, \( D_e \) the effective dispersion coefficient and \( S_i \) a sink/source term.

In this context diffusion is neglected.

The ADE is derived from a number of equations, which shall be briefly highlighted here. These equations are the conservation equation, advective (conversive) transport equations and diffusion/dispersion equations.
The conservation equation states that the change of total concentration of species $i$ ($c_{t,i}$) (adsorbed, precipitated and solute concentration) in a representative elementary volume is equal to the negative rate of change of the species flux ($J_i$) over depth minus any source/sink terms ($S$):

$$\frac{\partial c_{t,i}}{\partial t} = -\frac{\partial J_i}{\partial z} - S_i.$$  \hfill (3.7)

The solute transport is made up of three transport processes: advective flux ($J_a$), diffusive flux ($J_d$) and hydrodynamic dispersive flux ($J_h$).

$$J_i = J_a + J_d + J_h.$$  \hfill (3.8)

The advective transport is described the flow of water and the concentration of species $i$:

$$J_a = J_w \cdot c_i.$$  \hfill (3.9)

The velocity is not $J_w$, as the average pore water velocity ($\nu$) is greater than the Darcy velocity.

$$\nu = \frac{J_w}{\theta}.$$  \hfill (3.10)

As mentioned before diffusion is neglected in this context ($J_d = 0$) which leads us straight to dispersion. Dispersion can be described by a Fick’s law type equation:

$$J_h = -\theta \cdot D_e \frac{\partial c_i}{\partial z}.$$  \hfill (3.11)

The effective dispersion is dependant on longitudinal dispersivity ($D_L$) and the average pore water velocity:

$$D_e = D_L \cdot \nu.$$  \hfill (3.12)

If diffusion is considered the description of the effective dispersivity changes (which is as above mentioned of no concern here).

Because ideal tracers are crucial in determining transport parameters, the ADE for an ideal tracer will be given here. If water content does not change over time or length its formulation is:

$$\frac{\partial c_i}{\partial t} = \nu \cdot \frac{\partial}{\partial z} \left( D_L \frac{\partial c_i}{\partial z} - c_i \right).$$  \hfill (3.13)
3.2.2 Sorption

Sorption contains absorption and adsorption. Absorption is the process of assimilation of a substance by another (photons absorbed by water or the dissolution of CO₂ in water as H₂CO₃) [Stumm and Morgan, 1996]. Absorption is not considered in this work. Adsorption describes the interactions of substances at a surface [Merkel and Planer-Friedrich, 2008]. Adsorption is considered in this work. The most simple adsorption model is linear.

\[ q_i = k_{ad} \cdot c_i, \]  

(3.14)

where \( k_{ad} \) is the adsorption coefficient.

More complex models do exist and can be looked up in any literature covering the topic.

3.2.3 Dissolution and Precipitation

Dissolution and precipitation are modelled by thermodynamic principles which determine the equilibrium concentration of partaking substances for given chemical reactions. If the reaction time is big compared to the residence time in the system kinetic models need to be used to explain concentration-change over time. Kinetics describes how fast (or slow) equilibrium concentrations are reached. The thermodynamics of the chemical reactions are covered in this chapter, while the kinetics is described in Chapter 3.2.4.

Law of Mass Action

Any reversible chemical equilibrium or non-equilibrium reaction can be described by the law of mass action.

\[ aA + bB \leftrightarrow cC + dD \]  

(3.15)

Where a, b, c and d are stoichiometric coefficients for the number of moles partaking in the reaction. A and B are educts, C and D are Products. It has been observed that the concentrations of educts and products for a given reaction do occur in a defined ratio, if thermodynamic conditions are present. This is called the law of mass action and can be written as follows:

\[ K_{eq} = \frac{\{C\}^c \cdot \{D\}^d}{\{A\}^a \cdot \{B\}^b}. \]  

(3.16)

\( K_{eq} \) is the thermodynamic equilibrium constant of the reaction. Curly brackets \{\} indicate activity, as opposed to square brackets [ ], which indicate concentrations. The activity concept is elaborated in the next section.
Ion Activity

Ions in water do not behave ideally, this means chemical reactions stop at a point differing from what would be expected from concentration data for species involved in the reaction. To account for this non ideal behaviour the concepts of ionic strength and ionic activity have been introduced in science.

The ionic strength $I$ is described as

$$ I = \frac{1}{2} \sum c_i \cdot z_i^2, \quad (3.17) $$

where $c_i$ is the concentration of ion $I$ and $z_i$ the charge of the ion. With the ionic strength the activity coefficient $f_i$ can be calculated from the Debye-Hückel Equation (for solutions with ionic strength up to 5 mmol/L):

$$ \log(f_i) = -A \cdot z_i^2 \cdot \sqrt{I}. \quad (3.18) $$

$A$ is a temperature dependent constant or can be used as a fitting parameter for model evaluation, it is about 0.5 at 25°C in water. For solutions with ionic strength over 5 mmol/L (but lower than 100 mmol/L) the Extended Debye-Hückel Equation can be used.

$$ \log(f_i) = -A \cdot z_i^2 \cdot \frac{\sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} \quad (3.19) $$

$B$ is a temperature dependent parameter; it is about 0.33 in water at 25°C, $a$ is an adjustable parameter, corresponding to the ion radius (4Å for $SO_4^{2-}$, 6Å for Ca [Stumm and Morgan, 1996], [Lindsay, 1979]).

With the activity coefficient ($f_i$), activities ($a_i$) can be calculated.

$$ a_i = f_i \cdot c_i \quad (3.20) $$

3.2.4 Kinetics

Reactions that do not take place fast (i.e. reaction time $<<$ residence time in the system) are modelled by kinetics. Under different conditions different approaches are used.

General Approach

One advance used quite often is a first order model.

For a reaction

$$ A \leftrightarrow B + C, \quad (3.21) $$

where A, B and C are chemical species, the change of concentration of A can be written as:
\[
\frac{d[A]}{dt} = -k_{\text{kin}}[A].
\] (3.22)

\([A]\) is the concentration of species A and \(k_{\text{kin}}\) is the rate constant. The actual concentration of A over time \((t)\) then is

\[
[A] = [A_0] \cdot \exp(-k_{\text{kin}} \cdot t).
\] (3.23)

\([A_0]\) is the initial concentration. If more parameters do influence the process, the general equations can be supplemented with more terms to better describe a special problem. Parameters influencing kinetics are for example specific surface (m²/m³) or change of mass (and thereby specific surface) during the reaction.

**Precipitation/Dissolution**

To model precipitation and dissolution, the first order model can be adapted. To do this the saturation ratio (SR) of a reaction is used as the driving gradient. The SR is:

\[
SR = \frac{IAP}{K_{\text{eq}}},
\] (3.24)

where \(K_{\text{eq}}\) is the solubility constant described in chapter 3.2.3, and IAP is the ion activity product. If SR is greater than 1 the solution is oversaturated, if it is smaller it is undersaturated.

The difference between \(K_{\text{eq}}\) and IAP is that the activities in the IAP are actual activities at the moment, i.e. non-equilibrium activities, whereas the activities in \(K_{\text{eq}}\) are activities when equilibrium is reached. For a given reaction like Equation (3.15), the IAP is

\[
IAP = \frac{[C_j]^c \cdot [D]^d}{[A]^a \cdot [B]^b}.
\] (3.25)

With the SR the formulation for the concentration change follows.

\[
\frac{d[A]}{dt} = -k_{\text{kin}}(SR - 1)
\] (3.26)

This equation needs to be solved numerical to describe concentration as a function of time.

By coupling the equations for solute transport, adsorption, dissolution/precipitation and kinetics the system can be described numerical.
3.3 Gypsum

Gypsum is a crystalline substance composed of calcium, sulphate and water. The chemical formula is CaSO$_4$·H$_2$O, the molar mass is 172 g/mol. Gypsum is slightly soluble in water. Its dissolution is described by the following equation:

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}.$$  \hspace{1cm} (3.27)

The law of mass action written out for this equation is:

$$K_{\text{eq}} = \frac{\{\text{Ca}^{2+}\} \cdot \{\text{SO}_4^{2-}\} \cdot \{\text{H}_2\text{O}\}^2}{\{\text{CaSO}_4\}}.$$  \hspace{1cm} (3.28)

The activity for water is generally assumed to unity, as is the activity of solid substances. For gypsum dissolution equimolar concentrations of calcium and sulphate have to be present in solution. Solubility constants for gypsum can be found in the Literature. Stumm and Morgan (1996) listed the constant (log($K_{\text{eq}}$) = −4.58), as does Lindsay (1979) (log($K_{\text{eq}}$) = −4.64). Without considering activities this results in a saturation concentration for sulphate of 5.1 mmol/L (Stumm and Morgan) or 4.8 mmol/L (Lindsay).

If the ionic strength is considered, it has to be calculated.

$$I = \frac{1}{2}(c_{\text{Ca}} \cdot z_{\text{Ca}}^2 + c_{\text{SO}} \cdot z_{\text{SO}}^2),$$  \hspace{1cm} (3.29)

the concentrations for Ca$^{2+}$ and SO$_4^{2-}$ are set to 5.1 mmol/L (equilibrium concentration from Stumm and Morgan, without ionic strength), this results in an ionic strength of 20.5 mmol/L. With this ionic strength, activity coefficients can be calculated from the Extended Debye-Hückel Equation (3.19) (the extended equation has to be used as the ionic strength is greater than 5 mmol/L). The activity coefficients are 0.598 for Ca$^{2+}$ and 0.574 for SO$_4^{2-}$. The law of mass action (Equation (3.28)) together with the activity equation (3.20) gives:

$$K_{\text{eq}} = f_{\text{Ca}} [\text{Ca}^{2+}] \cdot f_{\text{SO}} [\text{SO}_4^{2-}].$$  \hspace{1cm} (3.30)

Because the concentrations of calcium and sulphate have to be equal (when equimolar dissolution is calculated for gypsum), the concentrations are:

$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = \sqrt{\frac{K_{\text{eq}}}{f_{\text{Ca}} \cdot f_{\text{SO}}}}.$$  \hspace{1cm} (3.31)

This results in concentrations of 8.75 mmol/L after calculating the ionic strength. These new concentrations again result in a changed ionic strength, for which new activity coefficients
have to be calculated, from which new concentrations are derived. This iterative procedure is repeated until the change of concentration is sufficiently small between calculation steps. In this case the calculation was repeated until the three leading digits were equal between calculation steps.

With this calculation the sulphate (and also calcium) concentration for equilibrium with gypsum is 10.3 mmol/L for the equilibrium constant given by Stumm and Morgan and 9.4 mmol/L for the constant given by Lindsay. This results in a gypsum solubility of 1780 mg/L (Stumm and Morgan) or 1620 mg/L (Lindsay), at 25°C and 1013 hPa.
4 Material and Methods

To investigate sulphur dynamics from technogenic soil substrate different methods were employed. The soil material was taken from a debris landfill site and used in percolation experiments. The percolated solution was analysed and a model was fitted to the results. In this chapter the methodology of the single steps will be described.

4.1 Experiments

This section explains how samples were obtained and how the experiments were carried out.

4.1.1 Soil Material

The material was gained from a profile in a depression of a middle-slope of the Teufelsberg. The slope is shown in Figure 4.1. The Teufelsberg is Berlin’s biggest debris landfill and a popular leisure time location for many Berliners. The profile was opened in a preceding research at the Teufelsberg. It was assumed that the material from the slope is ideally mixed by colluvial transport downhill. [Lahr et al., 2007]

![Figure 4.1 - Slope of the Teufelsberg](image)

4.1.2 Column Preparation

The column preparation was done in an earlier research. In that research the columns have already been percolated. This means that the original experiments were actually lengthened by the percolations undertaken in this study. No newly packed columns were used, but the results of the previous percolations were available and have been used. [Mekiffer, 2009]
The soil material from the Teufelsberg has been divided by sieving into fine soil (<2 mm) and two skeletal fractions (2 mm – 6.3 mm and 6.3 mm – 20 mm). The skeletal fraction > 6.4 mm was sorted by hand into different components. In Table 4.1 components and column numbers used in the experiments are listed. Also shown are the fractions of fine soil and skeletal component, as is the column length. [Mekiffer, 2009]

<table>
<thead>
<tr>
<th>Column number</th>
<th>Component</th>
<th>Mixture [%]</th>
<th>Length [cm] / Diameter [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fine soil</td>
<td>100</td>
<td>25 / 10.4</td>
</tr>
<tr>
<td>5</td>
<td>Fine soil and mixed skeletal components (2 mm – 6.3 mm)</td>
<td>90:10</td>
<td>25 / 10.4</td>
</tr>
<tr>
<td>9</td>
<td>Fine soil and red brick (6.3 mm – 20 mm)</td>
<td>90:10</td>
<td>10 / 10.4</td>
</tr>
<tr>
<td>10</td>
<td>Fine soil and plaster (6.3 mm – 20 mm)</td>
<td>90:10</td>
<td>10 / 10.4</td>
</tr>
</tbody>
</table>

Previous stirred batch tests showed sulphate concentrations of 104.4 mg/L (1.1 mmol/L) for the fine soil (1:2 soil/water ratio) [Mekiffer, 2010]

All columns were packed with a bulk density of 1.5 g/cm³. The soil material contains calcite. The mean sulphur contend of the fine soil is 0.07 % [Mekiffer, 2010]. In Figure 4.2 a soil column with the lower part of the disk permeameter (function is explained further on in the text) is shown.
4.1.3 Percolation

In this study the above mentioned four columns have been percolated. Column number 1 has been percolated twice. This results in five percolation experiments. An overview is shown in Table 4.2. The identifier contains the letter H, which is an abbreviation of the author’s name. This identifies the columns to be not part of previous experiments. Next part is the column number and in case of the second percolation of column one an “M” for mix eluate, the mix eluate is explained in the next paragraph, as is the role of the percolation solution in general.

<table>
<thead>
<tr>
<th>Number of Experiment</th>
<th>Identifier</th>
<th>Percolated Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H1</td>
<td>0.5 mM KBr and 1 mM KBr</td>
</tr>
<tr>
<td>2</td>
<td>H1M</td>
<td>0.5 mM KBr and Mixed Eluate</td>
</tr>
<tr>
<td>3</td>
<td>H5</td>
<td>0.5 mM KBr and 1 mM KBr</td>
</tr>
<tr>
<td>4</td>
<td>H9</td>
<td>0.5 mM KBr and 1 mM KBr</td>
</tr>
<tr>
<td>5</td>
<td>H10</td>
<td>0.5 mM KBr and 1 mM KBr</td>
</tr>
</tbody>
</table>

To quantitatively describe the hydraulic parameters of the columns an ideal tracer step signal was used. In experiments carried out previously, 0.5 mM KBr was used as a tracer substance. The step signal used in this research was a step from 0.5 mM KBr to 1 mM KBr. This step signal was used in all experiments except the second. In the second experiment column one was percolated with a mixture of already percolated solution to study any adsorptive effects of $\text{SO}_4^{2-}$ with the soil matrix.

To study effects of physical non-equilibrium and of time dependent sulphur solution, flow interruptions were introduced. Two flow interruptions were used, one of one day duration and a second of one week. This results in a general percolation scheme shown in Figure 4.3. The amount of percolated water was measured in pore volumes (PV). PV can also be used as a dimensionless temporal coordinate for outflow concentration results.
### Figure 4.3 - General percolation scheme, individual experiments differ from exact scheme

The percolation unit used is shown in Figure 4.4. For the experiment first the soil column is weighed, to determine the initial water content. Then it is placed on top of the sampler and the disk permeameter is put onto the column. The Disk permeameter contains a reservoir into which the percolation solution is filled. Also connected to the permeameter is a bubble tower which applies a defined suction to the soil surface. The pressure head used in this case was –8 cm water column. Beneath the soil column is a sampler on which the sample containers are placed. The sampler is placed in a box in which a defined subpressure (again –8 cm water column) is applied via a vacuum pump and another bubble tower (this results in unit gradient flow conditions). During the experiment each sample container collects approximately 70 mL of percolated solution before the next container is filled. When the experiment is over or if all containers are filled the vacuum box has to be opened. If the experiment is carried on, the new containers are put into the box and subpressure is applied again (which results in 3–5 min with a pressure head of 0 cm water column at the lower boundary).

The containers with solution are then weighed to determine the actual volume per container. pH and conductivity of the samples are measured. Afterwards the samples are stored to be analysed for ions later on.
4.2 Chemical Analysis

The samples were chemically characterized by measurement of pH, electric conductivity and cat- and anion analysis.

pH and conductivity were measured with a pH/conductivity-meter (WTW, inoLab, pH/cond, Level 1). The pH-meter was calibrated to the range from 4–9.

Later the cations were measured by atomic absorption spectrometry (AAS) (Perkin-Elmer 1100B, Atomic Absorption Spectrophotometer). Some of the samples had to be diluted to be in the measurement range.

For the anion analysis the samples were filtered over 0.45 µm membrane filters. Afterwards they were measured by ion chromatography (Dionex, AS 50 Autosampler, CD 20 Conductivity Detector, GP 50 Gradient Pump, AS 11 Anion-Exchange Column (4x250 mm), ASRS 300 Suppressor).

Form of Presentation

The measured concentrations of the chemical analysis can be plotted over experiment time to show temporal changes. The problem with this kind of presentation is that because of the flow interruptions (see Figure 4.3, p. 14) data is only acquired during flow periods. But the flow periods make up a very small portion of the over all experiment time (~ 11 days). To
circumvent this, the results are plotted over pore volumes (PV). One pore volume is the amount of water contained in the column.

\[ PV = V \cdot \theta \]  

(4.1)

As mentioned before the columns are not fully saturated, but a pressure head of \(-8\) cm water column is applied under flow conditions. This results in constant water content as soon as steady state is reached. Therefore the pore volumes were calculated with \(\theta(-8\) cm).

4.3 Numerical Modelling

Numerical modelling was carried out with HP1, a special module of the Hydrus 1D software, which uses PHREEQC, a chemical modelling software, to solve chemical equations. The three software packages will be briefly discussed here. The transport parameter estimation was done with CXTFIT, a spreadsheet tool; the kinetic and thermodynamic parameters were evaluated using the sum of squared errors (SSE), all this is elaborated in the last paragraph of this chapter.

The program settings are documented in the Appendix. Chapter 8.1, p. 45.

4.3.1 Hydrus 1D

Hydrus 1D is a program for numerical modelling of water and matter transport in saturated and unsaturated porous media. Further functions are implemented, but shall not be elaborated here. The flow and transport equations are solved by linear finite element schemes. Hydrus is limited if chemical dissolution/precipitation needs to be considered.

Hydrus has got a very elaborate graphical user interface (GUI) which guides the user through simulations. To model processes the user has to fill in the entire initial and boundary conditions as well as the process parameters into the GUI. The parameters needed to model the processes occurring in this research are listed in Chapter 3. The experiment conditions are described in Chapter 4.1.3.

Although at all times during the experiment unsaturated flow occurred, it is possible to simulate the flow as saturated. This is possible, because no redox reactions are modelled and therefore the gas phase needs not to be considered in the model. Further on only two flow conditions are present:

- No flow
- Unit gradient flow
Sulphur Release in Technogenic Soil Substrates

As we know this we can easily choose van Genuchten parameters ($\alpha$ and $n$) (Equation (3.2)) and van Genuchten-Mualem parameter ($k_s$) (Equation (3.5)), to fit the flow conditions measured. These parameters do not represent any real soil hydraulic properties, but are sufficient to simulate the encountered conditions.

4.3.2 PHREEQC

PHREEQC was developed for low temperature, aqueous, geochemical simulations. A wide array of reactions can be modelled with the code.

In the model applied here PHREEQC controls the chemical composition of the inflowing solution and of the solution in the modelled column. The inflowing solution is in equilibrium with the atmospheric CO$_2$ and O$_2$ and 0.5 mM KBr is dissolved. Because of the unsaturated conditions in the column the solution in the column is always equilibrated with atmospheric O$_2$. The gypsum solution and the concentrations of calcium and sulphate are governed by the law of mass action (Equation (3.16)) and by the kinetics of the solution. In this case the kinetics is described by the following equation [Hamann, 2011]

$$\frac{d[SO_4^{2-}]}{dt} = k_{\text{kin}} \cdot (1 - \text{SR}_{\text{gypsum}} \cdot K_{\text{new}}) \cdot \frac{m}{m_0}$$  \hspace{1cm} (4.2)

This equation is numerically integrated to calculate the sulphate concentration over time. The initial mass of the substance dissolved (in this case gypsum) is $m_0$, the actual mass at the time calculated is $m$. The term $m/m_0$ takes into account the changes in specific surface over reaction time. Reaction rates decline when the solid phase is dissolved and rise if solid phase precipitates. $K_{\text{new}}$ is a fitting parameter to adjust the solubility constant $K_{\text{eq}}$. This creates a new solubility constant ($K_{\text{eq}}^*$).

$$K_{\text{eq}}^* = \frac{K_{\text{eq}}}{K_{\text{new}}}$$  \hspace{1cm} (4.3)

In the program seven components make up the chemical system: H, O, C, Ca, S, K, Br. All the species encountered in the system are made up of these elements. The temperature dependence of the solubility product is always taken into account. The default setting for temperature in PHREEQC is 25°C, which was not changed (temperatures during experiments ranged from 19°C to 25°C). The thermodynamic data for the models is contained in a database. For the modelling in this work the standard PHREEQC database was used (phreeqc.dat). The solubility constant given for gypsum in the database is $\log(K_{\text{eq}}) = -4.58$. 

17.
4.3.3 HP1

As mentioned before the HP1 code couples Hydrus 1D and PHREEQC. For the modelling purpose the Hydrus GUI is used. PHREEQC input code just appears in very limited form. The coupled code has got some limitations though. Very important is that no inverse modelling (i.e. parameter estimation) is possible in HP1. If an automated parameter fitting should be done one would have to employ a separate program to do so.

4.3.4 Parameter Estimation

To determine transport parameters CXTFIT was used. CXTFIT is a spreadsheet tool, solving simple analytical problems of the ADE. Mean flow rates for the columns are determined from the experiment results. Dispersivity ($D_e$) is determined by fitting the ADE to the breakthrough curves of the ideal tracer ($\text{Br}^-$).

For thermodynamic and kinetic parameters parameter estimation was done by comparing the measured concentrations with modelled concentrations. This is done by using the sum of squared errors (SSE) as the objective function.

$$\text{SSE} = \sum_{j=1}^{j=k} (c_j - \hat{c}_j)^2.$$  \hspace{1cm} (4.4)

$c_j$ is the concentration in the $j$-th sample, $\hat{c}_j$ is the modelled concentration in the $j$-th sample.

Actually $j$ refers to the time of the experiment, when outflow of the sample occurred. This is of relevance as the flow rate during experiments varies, whereas the flow rate in the simulation is constant.

The concept for the model is described in the two previous paragraphs. Detailed information is given in Appendix 8.1, p. 45.
5 Results and Discussion

The first section of this chapter contains the experimental results, followed by the discussion of the experimental results in the second part. Afterwards the outcomes of the numerical modelling are shown, which are followed by the discussion of the numerical part.

5.1 Experiment Results

The results from the column experiments include physical properties of the columns (water flow velocity, water content and transport parameters) and chemical parameters of the percolated solution (pH, conductivity and concentrations of sulphate, bromide, calcium and magnesium). The results for the different experiments (see Table 4.2, p. 13) are discussed separately. The first experiment (H1) is discussed in detail, whereas for the others only results deviating from the results of H1 are shown. The full data collected during and after experiments can be found in Appendix 8.1 (p. 45).

For the purpose of more fluent reading the table covering the naming of the experiments and the column contents are repeated here. As mentioned before the column numbers are found in the experiment name. Table 5.1 lists the column specifications (Table 4.1, p. 12, repeated). The general flow scheme is repeated in Figure 5.1.

<table>
<thead>
<tr>
<th>Column number</th>
<th>Component</th>
<th>Mixture [%]</th>
<th>Length [cm] / Diameter [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fine soil</td>
<td>100</td>
<td>25 / 10.4</td>
</tr>
<tr>
<td>5</td>
<td>Fine soil and mixed skeletal components</td>
<td>90:10</td>
<td>25 / 10.4</td>
</tr>
<tr>
<td>9</td>
<td>Fine soil and charcoal</td>
<td>90:10</td>
<td>10 / 10.4</td>
</tr>
<tr>
<td>10</td>
<td>Fine soil and plaster</td>
<td>90:10</td>
<td>10 / 10.4</td>
</tr>
</tbody>
</table>
Values for volumetric water content, mean flow rate and mean pH during experiments are given in the text explaining the single experiments. They are also listed in Table 5.2.

### Table 5.2 - Recurring parameters measured during experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Volumetric Water Content [-]</th>
<th>Mean Flow Rate [mm/h]</th>
<th>Mean pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>0.318</td>
<td>46.4 ± 5.3</td>
<td>7.9</td>
</tr>
<tr>
<td>H1M</td>
<td>0.318</td>
<td>34.8 ± 6.5</td>
<td>7.9</td>
</tr>
<tr>
<td>H5</td>
<td>0.324</td>
<td>35.3 ± 32.9</td>
<td>7.8</td>
</tr>
<tr>
<td>H9</td>
<td>0.325</td>
<td>35.9 ± 14.1</td>
<td>7.9</td>
</tr>
<tr>
<td>H10</td>
<td>0.321</td>
<td>47.6 ± 11.5</td>
<td>8.0</td>
</tr>
</tbody>
</table>

#### 5.1.1 Experiment H1

The water content in the column was 674.5 mL, which results in a volumetric water content of 0.318. In Figure 5.2 the flow rates for the experiment are shown. The mean flow rate is 46.4 mm/h with a standard deviation of 5.3 mm/h.
Figure 5.2 - H1, column 1, flow rates during the experiment

The pH slightly increases during experiment over a range from 7.5 to 8.2, the mean proton activity \( \{H^+\} \) 1.3E-8 \((\text{pH} = 7.9)\), the standard deviation is 5.1E-9 (Figure 5.3).

Figure 5.3 - H1, column 1, pH of the percolated solution

In Figure 5.4 the concentrations of sulphate and bromide in the percolated solution are shown. The inflow concentration of bromide is also plotted. The first sample \((\text{PV} = 0.11)\) contained
high concentrations of sulphate and bromide \((SO_4^{2-} = 3.7\ \text{mmol/L}, \ Br^- = 4.7\ \text{mmol/L})\), which are not shown in the diagram. The sulphate concentration of the first sample after each flow interruption was higher than the following ones. Measurements after these first samples show that the sulphate concentrations are on a similar level (for three to four samples). After this they start to fall. For the first flow interruption it can be seen that the sulphate concentrations reach a rather constant levels after this decline. This is not to be seen for the second flow interruption, as the percolation ends before this might occur. Bromide concentration follows the step input. Later bromide shows a rise followed by a fall in concentration during the third flow period.

![Graph showing sulphate and bromide concentrations](image)

**Figure 5.4 - H1, column 1, sulphate and bromide concentrations of the percolated solution, bromide step signal for input is shown, the black lines indicate flow interruptions (1\textsuperscript{st} one day, 2\textsuperscript{nd} seven days)**

Magnesium concentrations were low during all experiments, calcium concentrations were higher (Figure 5.5). The calcium concentration of the first sample was 9.1 mmol/L; it is not shown in the diagram. The calcium measurements for the 3\textsuperscript{rd} flow period show a great deviation. Calcium concentrations are about one order of magnitude higher than sulphate concentrations.
Figure 5.5 - H1, column 1, calcium and magnesium outflow concentrations, flow interruptions are indicated by black lines

If the calcium and Magnesium concentrations are plotted logarithmic, some more information can be obtained (Figure 5.6). It can be seen that not only does the calcium concentration rise after flow interruptions, but also magnesium concentration. Both these concentrations show qualitatively similar concentration behaviour over time to sulphate.

Figure 5.6 - H1, column 1, logarithmic calcium and magnesium outflow concentrations, flow interruptions are indicated by black lines
5.1.2 Experiment H1M

H1M is the only experiment in which sulphate was contained in the inflow solution. The experiment H1M followed the experiment H1. Between the last day of H1 and the first day of H1M lie seven days. This means that experiment H1M could also be interpreted as a prolonging of H1.

The volumetric water content was 0.318. The mean flow rate in the experiment was 34.8 mm/h with a standard deviation of 6.5 mm/h. The average proton activity \( [H^+] \) was 1.3E-8 (pH = 7.9) with a standard deviation of 4.2E-9.

After 0.7 pore volumes flew out, input was changed from 0.5 mmol/L KBr to mixed eluate (containing the sulphate). Half of the breakthrough had passed after 1.7 pore volumes. The sulphur concentration in the outflow clearly shows the step input (Figure 5.7).

![Figure 5.7 - H1M, column 1, sulphate and bromide concentrations of the percolated solution, inflow concentration is shown as a dotted line, black lines indicate flow interruptions, grey lines indicate sulphate input and break through](image)

5.1.3 Experiment H5

Column five contains all skeletal components. The volumetric water content was 0.324. The column dropped to the floor between day one and day two of the experiment. This changed the flow regime, which can be seen in Figure 5.8. The average flow rate was 35.3 mm/h with a standard deviation of 32.9 mm/h.
Due to the lowered flow rates the percolation at the last day was not finished and carried on the next day. This results in three flow interruptions, the first for one day, the second for seven days and the third for one day.

The mean proton activity \( \{H^+\} \) was 1.5E-8 (pH = 7.8) with a standard deviation of 6.9E-9.

As already seen in the other columns, the first samples (PV = 0.11) contained very high amounts of solutes. The first values for sulphate were 5.4 mmol/L and 3.1 mmol/L, they are not shown in Figure 5.9.
**Sulphur Release in Technogenic Soil Substrates**

![Graph](image)

**Figure 5.9** - H5, column 5, concentrations of sulphur and bromide, flow interruptions are indicated by black lines.

### 5.1.4 Experiment H9

Column nine contains fine soil and skeletal charcoal components. The volumetric water content was 0.325. The mean flow rate was 35.9 mm/h with a standard deviation of 14.1 mm/h. The mean proton activity \( [H^+] \) was 1.2E-8 (pH = 7.9) with a standard deviation of 2.0E-9.

The bromide and sulphate concentrations show results comparable to the other columns, although it can be noted that the values after the 2nd flow interruption do not decrease immediately (Figure 5.10). Bromide break through occurs after about 1 PV. Due to the smaller volume of column nine (and ten) less measurements were made (the amount of solution needed for analysis remained the same, whereas the pore volume was smaller).
As seen in the other columns the first value for sulphate (PV = 0.25) was quite high (3.4 mmol/L) and is not shown in the figure.

5.1.5 Experiment H10

Column ten contains fine soil and skeletal plaster components. The volumetric water content was 0.321. The mean flow rate was 47.6 mm/h with a standard deviation of 11.5 mm/h. The mean proton activity \( \{H^+\} \) was 1.0E-8 (pH = 8.0) with a standard deviation of 1.8E-9. The bromide and sulphate concentrations show results comparable to the other columns (Figure 5.11). Bromide break through occurs after about 1 PV. Due to the smaller volume of column ten less measurements were made (the amount of solution needed for analysis remained the same, whereas the pore volume was smaller).
5.2 Discussion of Experiments

The predicted pH for a system of CaO – CO$_2$ – H$_2$O – H$_2$SO$_4$ with a partial pressure of 0.0003 atm CO$_2$ is 7.8 [Lindsay, 1979]. If more chemical components are present, slightly different pH values may occur. The pH for a pure CaO – CO$_2$ – H$_2$O system with a partial pressure of 0.0003 atm CO$_2$ would be 8.3 [Lindsay, 1979].

The pH of all experiments oscillated around 7.9. This underlines that a system containing calcite and gypsum is present.

If physical non-equilibrium (transport limitation) would occur, one would see steps in the bromide concentrations when flow interruptions took place. As this is not the case it can be assumed that diffusion into and out of dead end pores and aggregates is negligible. The delay between bromide input and outflow step shows that the estimation of pore volumes is approximately correct (the end of the input step should be one pore volume before half of the break through curve, [Br$^{-}$] = 0.75 mmol/L). The dispersivity was calculated from the bromide break through curve, this is elaborated in Section 5.3 (p.30).

During experiment H1 bromide concentration showed a peak during the third flow period (Figure 5.4, p. 22). This is attributed to the fact, that between the second and the third flow period the column as poorly covered, which permitted relatively high evaporation rates, so that bromide was concentrated in solution, which is seen in the outflow.
In all experiments first flush effects were observed. This means that the first samples of the percolation show significantly higher concentrations than the later samples. If a column dries large parts of the soil solution evaporate, this means that the concentration in the solution is raising. With this high concentration precipitation or sorption occurs (whichever model is applied/fits best). When water is reintroduced to the column dissolution/desorption takes place and results in high concentrations of chemical components. This also happens (but to a lesser degree) when flow interruptions take place. Although the columns were covered with aluminium-foil some evaporation took place. This means that the first samples after a flow interruption also show relatively high concentrations. For experiment one the samples following these show a concentration plateau (see Figure 5.4, p. 22), which is attributed to the fact that these samples consist of solution which was inside the column during flow interruption and is then displaced by new inflowing solution. This results in a break through curve for sulphate (or rather for inflowing solution just saturated during flow period). For the second flow period, after the break through the sulphate concentration reaches a constant level. This represents the flow equilibrium concentration. These effects can (to a lesser extend) also be observed in the other columns. But one has to keep in mind, that for columns nine and ten the ratio pore volume/sample volume is much smaller (due to the smaller column length).

From Figure 5.6 (p. 23) it can be seen that calcium and magnesium concentrations show qualitatively the same behaviour as sulphate. This is not surprising as calcium and magnesium do occur associated with sulphate in soils. The height of the calcium concentration (~ ten times higher than sulphate) remains unclear. It was theorized that calcite is dissolved by carbonic acid and this is the reason for the high concentrations. This has not yet been tested for plausibility by calculations.

Adsorption of sulphate could not be observed during experiment H1M (Figure 5.7, p. 24). If relevant adsorption happened, retardation of sulphate should be seen in the diagram. This is not the case as between inflow of mixed eluate and break through lies one pore volume. This shows no retardation of sulphate.

The sulphur concentrations in all samples are low (highest value: 5.47 mmol/L (H5), Figure 5.9, p. 26) compared to the theoretical solubility of 10.4 mmol/L (see Chapter 3.3, p. 9). And the highest values appeared during first flush, when columns were dried out after previous percolations. The average value during percolation was an order of magnitude below the theoretical solubility. Even after flow interruptions values were in this low range.
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Sudmalis and Sheikholeslami (2001), found that “co-precipitation resulted in CaCO$_3$ crystals interwoven by CaSO$_4$ crystals. This tends to result in a co-precipitate that is stronger than pure CaSO$_4$ and weaker than pure CaCO$_3$ precipitate.” This means that if dissolution occurs the solubility of gypsum is inhabited by calcite. This gives an explanation for the very low sulphur concentrations found during experiments in spite of large calcium concentrations. The quantitative effects of this have been studied using the numerical models introduced already. This leads us to the following passage in which these results are presented and discussed.

5.3 Modelling Results

The ADE was fitted to all bromide breakthrough curves. Using the results of experiment one (H1) as boundary conditions, a sensitivity study was undertaken to clarify which parameters have great influence on the model. And which parameter set gives the best fitting results. The parameters varied were $K_{eq}$ (solubility constant) and $k_{kin}$ (rate constant). No code or algorithms were used for the parameter fit. The experiment containing sulphate inflow (H1M) was not modelled as it was solely undertaken to investigate sorption effects. For the other columns forward modelling was undertaken with the parameter-set found for H1.

5.3.1 Transport Parameters

The transport parameters were determined by fitting the ADE to the bromide breakthrough curves of each single column. The longitudinal dispersivities found for the columns are listed in Table 5.3.

Table 5.3 - Longitudinal dispersivities of the different columns

<table>
<thead>
<tr>
<th>Experiment</th>
<th>H1</th>
<th>H5</th>
<th>H9</th>
<th>H10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_L$ [mm]</td>
<td>5.7</td>
<td>24.0</td>
<td>29.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 5.12 shows the breakthrough for column one. The time axis shows the time during which flow occurred. Flow interruptions are not shown in this depiction. This is legitimate as flow interruptions did not have an effect on bromide concentrations. The ADE fits the data well.
Figure 5.12 - Column one (H1), break through curve and fitted ADE

For column five the fit of the ADE to the data was not possible well (Figure 5.13). Due to the high irregularities in the flow conditions (Figure 5.8, p. 25) the assumptions needed for the analytical solution of the ADE (steady state water flow) were not fulfilled. The longitudinal dispersivity was calculated using only the second part of the break through curve (where bromide concentrations were falling). Even so the plateau concentration of bromide was lower for measurements than predicted with the ADE.
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Figure 5.13 - Column five (H5), breakthrough curve and fitted ADE

For column nine the simulated concentrations do not represent the plateau concentration for bromide (Figure 5.14). A mass balance problem occurs as less bromide is forecast with the model than is actually present in the column. The parameter varied (longitudinal dispersivity) does not result in a good fit.

Figure 5.14 - Column nine (H9), breakthrough curve and fitted ADE
The qualitative concentration behaviour for column ten is described well by the ADE (Figure 5.15). As seen for column nine, the mass balances of the modelled concentrations and of the measured concentrations do not match. But as the qualitative behaviour is matched this does not change results for longitudinal dispersivity.

![Figure 5.15 - Column ten (H10), breakthrough curve and fitted ADE](image)

### 5.3.2 Sensitivity Study (H1)

The average flow rate \( (J_w) \) for H1 was 46.4 mm/h, the longitudinal dispersivity was 5.7 mm (which is a rather small value for a 250 mm column).

A crucial part for the simulation is the initial concentration inside the column. The initial concentration in the columns was set to a value according to concentration in the first samples. Because the equilibrium constant \( (K_{eq}) \) was changed, this results in precipitation of gypsum. Dependent on dispersivity a volume of over one pore volume is needed to displace all of the initial solution from the column (the theory states that after one pore volume half of the breakthrough curve for the inflowing solution has passed). After this flow equilibrium is reached and the initial concentration is not influencing the further simulation any more.

The starting values of \( K_{eq} \) and \( k_{kin} \) were determined by an educated guess, and than fitted by nearing the “real” values. When roughly fitting values were found a parameter-mesh was used to calculate values for the objective function (which was the SSE). The process is elaborated on the next pages.
Parameter estimation was undertaken using time coordinates. This results in a model output shown in Figure 5.16.

![Graph showing measured and modelled concentrations of sulphate over time.](image)

**Figure 5.16 - Measured and modelled concentration of sulphate over time (log($K_{eq}$) = −7.53, $k_{kin}$ = 2.0E−5 mol/cm³/h)**

This form of presentation does not show what actually happens during flow periods and large parts of the modelled concentrations shown are in data free space. As mentioned before the time coordinate can be transformed into pore volumes (Chapter 4.2, p. 15, Equation (4.1)). If this is done only flow periods are depicted (Figure 5.17). Because modelling was undertaken using time coordinates and an average flow rate to compare the models, the representation over pore volumes shows differences between the flow interruptions from the experiments and the modelled flow interruptions. This could be corrected by using average flow rates for individual flow periods rather than for the whole duration of the experiment.
By varying the equilibrium constant ($K_{eq}^*$) and keeping the rate constant ($k_{kin}$) to a fixed level it can be seen that $K_{eq}^*$ changes equilibrium concentration (Figure 5.18). Equilibrium concentration occurs when the solute is inside the columns long enough for the kinetic reaction to reach equilibrium (residence time >> reaction time). In the graphs the equilibrium concentration is the concentration at the beginning of the second and third flow period. $K_{eq}^*$ also influences the flow equilibrium concentration (seen at the end of a flow period).
Figure 5.18 - Modelled concentrations for different equilibrium constants, with fixed rate constant

The rate constant \((k_{\text{kin}})\) influences the flow equilibrium level (seen at the end of flow periods).

By comparing the squared sum of errors (SSE) of the different sets of parameters the best fit from the parameter-set can be found (Figure 5.20). The best fitting values are \(\log(K_{\text{eq}}^*) = -7.53\) and \(k_{\text{kin}} = 2.0E-5\text{ mol/cm}^3\text{/h}\).
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Figure 5.20 - Sum of errors squared over rate and equilibrium constant

For the SSE only the second and third flow period was taken into account (because of the initial concentrations, which were not part of the parameter adjusting). The first values from flow periods were not taken into the calculation, because of first flush effects (discussed in Chapter 5.2, p.28). The SSE values are also shown in Table 5.4. The minimum value is 0.0289 (log($K_{eq}$) = -7.53, $k_{kin} = 2.0E-5$ mol/cm³/h).

Table 5.4 - SSE values for different log($K_{eq}$*) and $k_{kin}$

<table>
<thead>
<tr>
<th>SSE</th>
<th>log($K_{eq}$*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-7.36</td>
</tr>
<tr>
<td>$k_{kin}$ [mol/cm³/h]</td>
<td>$k_{kin}$ [mol/cm³/h]</td>
</tr>
<tr>
<td>1.0E-05</td>
<td>0.0708</td>
</tr>
<tr>
<td>1.5E-05</td>
<td>0.0648</td>
</tr>
<tr>
<td>2.0E-05</td>
<td>0.0707</td>
</tr>
<tr>
<td>2.5E-05</td>
<td>0.0879</td>
</tr>
</tbody>
</table>

The modelled concentration for the best fitting parameter set is depicted in Figure 5.17, p. 35.

5.3.3 Forward Modelling

From column experiment one (H1) the values for the equilibrium and the rate constant were taken and transferred to the other columns. The results of this are found in this section.
**Column five (H5)**

The mean flow rate for the experiment was 35.3 mm/h and longitudinal dispersivity 24 mm. Parameters for the model were \( \log(K_{eq}^*) = -7.53 \) and \( k_{kin} = 2.0E-5 \text{ mol/cm}^3/\text{h} \). Due to the change of flow rates during the experiment (see Figure 5.8, p. 25) the averaged flow rate does not exactly represent the flow regime inside the column. The sulphate concentrations in the outflow were much higher than would be expected from the model prediction based on experiment one (Figure 5.21).

![Figure 5.21 - Modelled and measured sulphate concentrations for column five](image)

**Column nine (H9)**

The flow rate for the experiment was 35.9 mm/h and longitudinal dispersivity of 29.5 mm. Parameters for the model were \( \log(K_{eq}^*) = -7.53 \) and \( k_{kin} = 2.0E-5 \text{ mol/cm}^3/\text{h} \). Outflow concentrations were higher than the model predicted.
Column ten (H10)

The flow rate for the experiment was 40.3 mm/h and longitudinal dispersivity of 3.2 mm. Parameters for the model were log($K_{eq}^*$) = −7.53 and $k_{kin}$ = 2.0E-5 mol/cm³/h. Outflow concentrations were higher than the model predicted (Figure 5.23).

Figure 5.22 - Measured and modelled sulphate concentrations for column nine

Figure 5.23 - Measured and modelled sulphate concentrations for column ten
5.4 Discussion of Modelling

It has been shown that it is possible to apply a precipitation/dissolution model to the problems encountered in the system, to qualitatively describe concentration over time. This would not have been possible if adsorption models were applied. The concentrations found were described and predictions of system behaviour in the field applying this knowledge are possible.

The changing flow rates during the experiments were not represented well in the models with the averaged flow rates applied. This does not influence the quality of the model; it only affects the depiction in the figures. Averaged flow rates for single flow periods could be calculated to better represent actual flow rates. The data would also permit high resolution flow rate changes down to the level of time intervals between sample collections (~ 10 min).

The sensitivity study (Chapter 5.3.2, p. 33) resulted in quantitative description of \( K_{eq}^* \) and \( k_{kin} \). \( \log(K_{eq}^*) \) is \(-7.53\), which is roughly a factor 1,000 smaller than literature values (-4.58 [Stumm and Morgan, 1996] and -4.64 [Lindsay, 1979]).

If the calculations from Chapter 3.3 (p. 9) are used this lowered equilibrium constant leads to an equilibrium concentration for sulphate and calcium of 0.19 mmol/L and a solubility of gypsum of 33.4 mg/L.

Due to the changed equilibrium constant of gypsum the model predicted precipitation inside the column for the first modelled hours of the experiment. This is the case because the initial concentrations inside the column (as starting conditions) were set to values according to the concentrations measured in first samples. These samples show concentrations of sulphate and calcium below gypsum saturation (~ 5 mmol/L). In this concentration range no precipitation of gypsum occurs. As the changed equilibrium constant only represents the effect of inhibited dissolution via co-precipitation it is of no use to incorporate the effect of high sulphate concentrations occurring due to first flush (discussed in Chapter 5.2, p. 28). In fact the changed equilibrium constant causes the model to predict precipitation of gypsum. This is false. But it has no effect on the predicted concentrations after equilibrium or flow equilibrium is reached the first time during the modelled experiment. The only effect is that the gypsum concentration inside the column is overestimated. But if the time until no more sulphate is leached from the column should be modelled the initial concentration is paramount.

In columns five (H5) and nine (H9) the equilibrium concentration is not as low as estimated from the model set up with the data of column one. Nonetheless the concentrations are far below the theoretical solubility of 10.3 mmol/L [Stumm and Morgan, 1996] and 9.3 mmol/L.
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[Lindsay, 1979] (Figure 5.21, p. 38 and Figure 5.22, p. 39). The same can be said to a lesser extend for column ten (H10) (Figure 5.23). The heightened concentrations from column five and nine could be the result of the addition of the mixed skeletal components (column five) and the red brick components (column nine), but it is not possible to proclaim this with no parallel column experiments existing.

Kuechler et al. (2004) found gypsum dissolution rate constants of 3.96E-4 mol/cm²/h, this is one order of magnitude higher than the constant found here ($k_{\text{kin}} = 2.0E-5$ mol/cm²/h). Kuechler et al. (2004) did take the specific surface of the dissolution process into account (m² of reactive surface per m³ of reaction volume), in this study the specific surface was described as part of the rate constant (reflected by the cm³ in the denominator of the unit (see Equation (3.23) and (4.2)). The lessened rate constant does not surprise as co-precipitates of calcite and gypsum are assumed. It is theorised that these co-precipitates inhibit the rate of dissolution of gypsum. Because of the interwoven character of calcite and gypsum crystals [Sudmalis and Sheikholeslami, 2000] the calcite crystals diminish the accessibility (active surface) of the gypsum crystals. Jeschke at al. (2001) on the other hand reported dissolution rates in the order of $4E-5$ mol/cm²/h, which is well in accordance with the measurements here.

It can be seen, that sulphate concentrations are higher after seven day flow interruption than they are after one day flow interruption. This fact itself does not surprise, as one can well imagine that slow kinetics sets free sulphate at low rates for long periods. These slow kinetics could be the result of non-gypsum sulphate components in the soil or of dissolution sites with limited accessibility. The point is that the model is not able to describe this effect. If lowered rate constants are applied the flow equilibrium concentration goes down. Actually three points do exist in the figures, which must be hit by the model. These points are the flow equilibrium and the concentration values after one and seven day flow interruptions. This leads us to errors caused by bad fit and errors caused by the model. Errors caused by a bad fit are well researched and many tools (which have not been employed in this study) do exist to minimize these. Errors caused by the model, i.e. by a bad or wrong description/understanding of the system can not be corrected via automated tools. Process understanding is the resource needed here. To describe the heightened concentrations at the beginning of the third flow periods a model employing two kinetics (representing two different sorption sites) would be able. Such a model would need four parameters to describe two first order kinetics (two equilibrium concentrations and two rate constants). As only three points defining kinetics do exist, this is not possible with the data present.
If one now makes a step back and observes the initial problem once more, it can be noted that the batch experiment results ([SO$_4^{2-}$] = 1.1 mmol/L) describe leaching concentrations quite well. Especially if residence times in the Teufelsberg are considered (>30 a, with a profile depth of 50 m, groundwater recharge of 150 mm/a and water content of 10% (conservative estimate for field capacity)).
6 Conclusion

With the experiments carried out and the model developed it is possible to qualitatively describe sulphate leaching from the soil columns. The models to achieve this description employed kinetics and changed thermodynamic equilibrium, no adsorption was needed. It has been shown, that the equilibrium constants for the concentrations modelled in the columns are three orders of magnitude smaller than the ones given in the literature for pure gypsum. It is theorized that co-precipitates of calcite and gypsum are the cause of these lowered constants. These co-precipitates form structures of interwoven crystals.

As indicated in Chapter 5.4, it would be useful to employ a two kinetics model to describe the concentration curves. The two kinetics represent sites with comparable fast dissolution of gypsum and sites with slower rates. To circumvent the problem of missing data (discussed in Chapter 5.4) an easy way would be to undertake some stirred batch tests and use these values as equilibrium concentration for the second (slower) first order kinetic. With the mechanical energy introduced via stirring it should be possible to reach sites with limited accessibility in reasonable time. For further model calibration it would be useful to carry out a set of parallel column experiments.

With the parameters found during this work it is possible to attempt a simulation for a 50 m soil column, representing the Teufelsberg. This would of course be a very rough estimation. Problems to be considered are how well the fine soil from the middle slope does represent the makeup of the whole landfill and how to quantify the influence of debris (containing boulders of up to meters in diameter) on flow conditions. Physical non-equilibrium does not influence processes in the columns used in the study. It has not been tested whether this holds true for sulphate transport under field conditions.
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8 Appendix

8.1 HP1 Settings

In this Appendix screenshots of the settings for HP1 used to model the columns are printed. The screenshots here apply to column ten, but can be transferred to the other columns.

Figure 8.1- General Project Overview, all fields in which input is needed are shown (left part of the window, “Pre-processing”)
Figure 8.2 - Main Process, water flow is modelled, as is solute transport (via PHREEQC).

Figure 8.3 - Geometry Information, column size is specified.
Figure 8.4 - Time Information, duration of the experiment and number of time variable boundary conditions (number of changes in boundary condition, e.g. flow interruptions)

Figure 8.5 - Print Information, controls amount of data output
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Figure 8.6 - HP1 - Print and Punch Controls, settings chosen after HP1 Tutorial [Jacques and Šimůnek, 2009]

Figure 8.7 - Iteration Criteria, unchanged
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Figure 8.8 - Soil Hydraulic Model, van Genuchten – Mualem model is chosen

Figure 8.9 - Water Flow Parameters, parameters are specified to fit the desired flow rate in the experiment, the parameters were not determined for different pressure heads
Figure 8.10 - Water Flow Boundary Conditions, boundary conditions are specified via the suction applied in the experiments.
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Figure 8.11 - Solute Transport, seven solutes were chosen, this is important for PHREEQC in the next screen.

Figure 8.12 - HP1 Components and Database Pathway, atomic species to be considered are specified, reduction stat of redox-sensitive elements has to be given.
Figure 8.13 - HP1 - Additions to Thermodynamic Database, rate equations for gypsum are given (written in basic)

Figure 8.14 - HP1 - Definition of Solution Compositions, starting and boundary solution are defined
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Figure 8.15 - HP1 - Geochemical Model, amount of gypsum in the column (mol/L of soil), kinetic parameters

Figure 8.16 - HP1 - Additional Output, defines for which species output is generated
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**Figure 8.17 - Solute Transport Parameters**, bulk density was known, dispersivity has been determined by fitting the ADE to the breakthrough measurements of Br–

**Figure 8.18 - Solute Transport Boundary Conditions**, inflow concentrations given in flux, lower boundary conditions defines, that no transport back into the column is possible
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Figure 8.19 - Time Variable Boundary Conditions, times of flow interruptions are given here

<table>
<thead>
<tr>
<th>Time [hours]</th>
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<th>GWL [cm]</th>
<th>oTop</th>
<th>oBot</th>
</tr>
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<td>3001</td>
</tr>
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<td>-8</td>
<td>-8</td>
<td>3001</td>
</tr>
</tbody>
</table>

Figure 8.20 - Profile Information – uniform pressure head of ~8 cm water column is applied in the whole profile
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Figure 8.21 - Profile Information – one observation point is inserted at −25 cm